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SO₂ Oxidation across Marine V₂O₅-WO₃-TiO₂ SCR Catalysts – A Study at Elevated Pressure for Preturbine SCR Configuration

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Abstract

The undesired oxidation of SO₂ was studied experimentally at elevated pressures of up to 4.5 bar across two commercial vanadium (1.2wt% and 3 wt% V₂O₅) based Selective Catalytic Reduction (SCR) catalysts. This pressure range, is of interest for preturbine SCR reactor configuration for NO_x reduction on ships. The residence time in the catalyst was kept constant, independent on pressure, by adjusting the total flow rate. The conversion of SO₂ was of the order 0.2-3 % at temperatures of 300-400°C and was independent of the pressure. Based on the measured conversion of SO₂, the kinetics were fitted using a nth order rate expression. The reaction order of SO₂ was found close to one, and the reaction order of SO₃ was found close to zero, also at increased pressures of up to 4.5 bar. The rate of SO₂ oxidation was clearly promoted by the presence of 1000 ppm NO_x at elevated pressure, however, at atmospheric pressure the effect was within experimental uncertainty. The promoting effect is explained by a catalyzed redox reaction between SO₂ and NO₂, and since more NO₂ is formed at elevated pressure, a higher degree of promotion by NO_x is observed at elevated pressures.

Keywords

SO₂ oxidation; Pressurized SO₂ oxidation; preturbo SCR configuration; SCR of NO_x on Ships; SO₃ formation;

1 Introduction

In today's shipping industry, more than 90% of oceangoing vessels are powered by diesel engines burning fossil fuels¹. Emissions, such as nitrogen oxides (NO_x) and sulfur oxides (SO_x) contribute to the acidification of the sea and land and also reduced air quality in harbor cities². Around 70% of the emissions from ships are produced within 400 km. of land, and the shipping industry contributes to approximately 15% of the global anthropogenic NO_x and 5-8% of the global SO_x emissions^{3,4}. Consequently, limitations of NO_x and SO_x emissions are targeted through the introduction of Marpol 73/78 Annex VI Tier III regulation 13 and 14⁵.

The new Tier III, regulation 13, is an approximate 75% NO_x reduction, compared to the earlier IMO Tier II regulation (Jan. 2011) as shown in **Fig. 1**. Tier III compliance is required for all ships built after 1. January 2016 when sailing within NO_x Emission Control Areas (NECA's), such as the Baltic Sea or in the North Sea⁵. Marpol 73/78 regulation 14 states the maximum allowed sulfur content in the fuel onboard a ship which depends on whether the ship is operated in- or outside of a SO_x Emission Control Area (SECA). Regulation 14 requires maximum 0.1 wt% S within SECA's but also states that a higher sulfur content is allowed, as long as the sulfur emissions are reduced to at least the same extent as if a low sulfur fuel was used⁵.

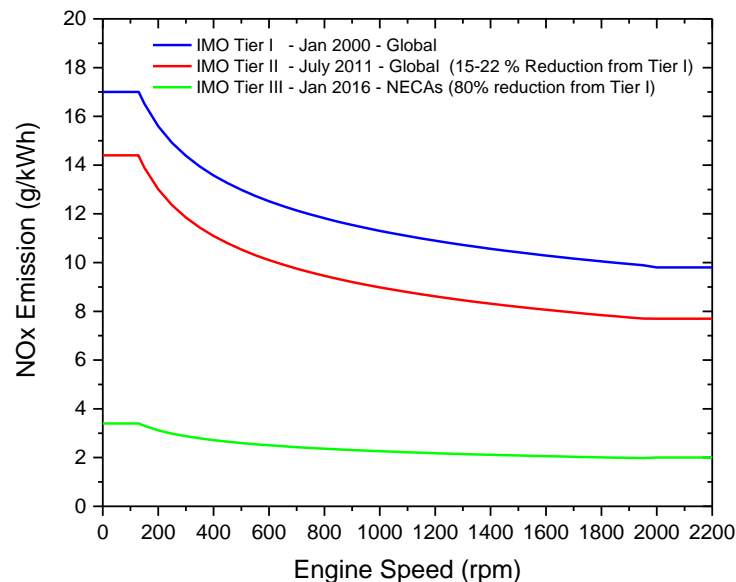
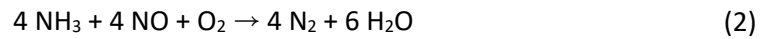
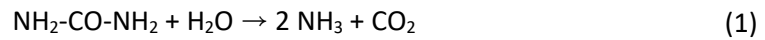


Fig. 1 Allowed NO_x emissions as a function of engine speed according to Marpol 73/78 Annex VI Regulation 13⁵

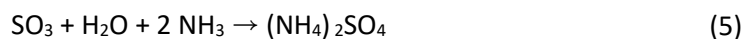
The NO_x compliance to IMO Tier III is expected to be achieved through either Exhaust Gas Recirculation (EGR), use of dual-fuel engines, or by the implementation of Selective

Catalytic Reduction (SCR) of NO_x⁶. EGR is a primary NO_x reduction method, in which the production of NO_x from the engine is reduced by lowering the combustion temperature and oxygen content through recirculation of exhaust gas (increased H₂O and CO₂ inside the combustion chamber)¹. SCR, on the other hand, is a secondary NO_x reduction method, in which the NO_x emissions are reduced downstream of the engine, by introducing a catalytic reactor in the exhaust gas aftertreatment system.

SCR of NO_x is a well-known technology, which has been used on both stationary and mobile sources to reduce NO_x emissions since the 1980s⁷⁻⁹. NO_x emissions from mobile units, such as ships, are reduced across a catalyst by introducing a 30-40 wt% aqueous solution of urea usually sprayed into the exhaust gas as small droplets upstream of the catalyst¹⁰. The droplets evaporate and decompose into ammonia and CO₂ according to reaction (1). Ammonia then reacts with oxygen and NO_x across the catalyst forming harmless nitrogen and water, according to reaction (2) resulting in a NO_x reduction of usually 80-95 % at temperatures of 300-450 °C¹⁰.



The catalyst used for SCR of NO_x on ships is usually the ternary vanadium based (V-SCR) catalyst, doped with tungsten on a carrier of titanium dioxide (V₂O₅/WO₃/TiO₂)¹¹⁻¹³. The V-SCR catalysts are well known for not being deactivated by the high SO₂ concentrations, up to 1000 ppm, present in marine diesel exhaust gas¹⁴⁻¹⁶. The oxidation of SO₂ according to reaction (3), is also slightly activated by a V-SCR catalyst, usually resulting in an SO₂ oxidation of 1-3% under SCR operating conditions¹⁷. This reaction is critical to study because the produced SO₃ readily reacts with water forming sulfuric acid causing corrosion, or it can further react with ammonia forming ammonium bisulfate (ABS) or ammonium sulfate (AS) according to reaction (4) and (5) respectively¹⁸⁻²⁰.



The formed sulfates may condense when the exhaust gas temperature decreases. The condensation of sulfates within the catalyst pore system is a particular problem, since capillary forces result in a higher dew point temperature than in the bulk, and therefore a higher temperature is needed to ensure that the catalyst is not deactivated^{20,21}. The specific dew point temperature depends on both the concentrations of NH_3 , H_2SO_4 , and the pore sizes²⁰. With a high sulfur fuel (e.g., 3.5 wt% sulfur) the catalyst must, therefore, be placed at temperatures above 330-340°C^{11,22}. However, if a low sulfur fuel is used instead (e.g., 0.1 wt% of sulfur) a lower temperature of 260°C can be used, without deactivating the catalyst²². In two-stroke marine diesel engines such high temperatures are only continuously achievable by installing the catalytic reactor upstream of the turbocharger, where a pressure of up to 4.5 bar is present¹¹. The higher pressure will increase the condensation temperature²³ and could affect the oxidation of SO_2 .

Earlier studies of SO_2 oxidation²⁴⁻²⁶ have reported that the rate of SO_2 oxidation has a zero order oxygen dependency at concentrations above 1-2 vol%, which is the case for marine diesel engines exhaust gas ($\text{O}_2 > 10 \text{ vol}\%$ ^{1,27}). Water has been reported to inhibit the rate of SO_2 oxidation²⁵, however, at practical water concentrations (5-15%) the rate is found to be independent of the water concentration. The reaction is commonly reported to be first order in SO_2 ²⁸⁻³⁰, while the reported SO_3 orders range from negative first order²⁴ to a zero order dependency²⁸⁻³⁰. Earlier studies have all been carried out at atmospheric pressure. Therefore this study will expand upon the current knowledge of catalytic SO_2 oxidation to high pressure marine conditions, using two commercial $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$ catalysts supplied by Haldor Topsøe A/S. The effect of temperature, pressure, SO_2 concentration, and NO_x concentration is presented.

2 Experimental Methods

2.1 Apparatus

The setup used for measurements of pressurized SO_2 oxidation is shown schematically in **Fig. 2**. Nitrogen, air, and liquid water were added to the first heater (HE1) using Brooks Smart Mass Flow Controllers (MFC's) for gas addition and Brooks liquid mass Flow model 5882 for addition of water. Water was evaporated in the first heater, a second heater (HE2) was used to control the reaction temperature in the range of 290-420 °C, and heating elements around the reactor helped to maintain the reaction temperature. A

manual backpressure valve was used to control the reaction pressure to between 1-4.5 bar. Gaseous SO_2 was added to the hot gas and passed through a static mixer from Sulzer, before reaching the reactor. The standard experimental conditions were: 5% H_2O , 8-10% O_2 , and approximately 1000 ppm of SO_2 in N_2 as shown in **Table 1**, and in some experiments, 1000-1500 ppm of NO_x was also added to the flue gas before the mixer, as with SO_2 . Isothermal conditions were verified by K-type thermocouples placed before and after the catalyst.

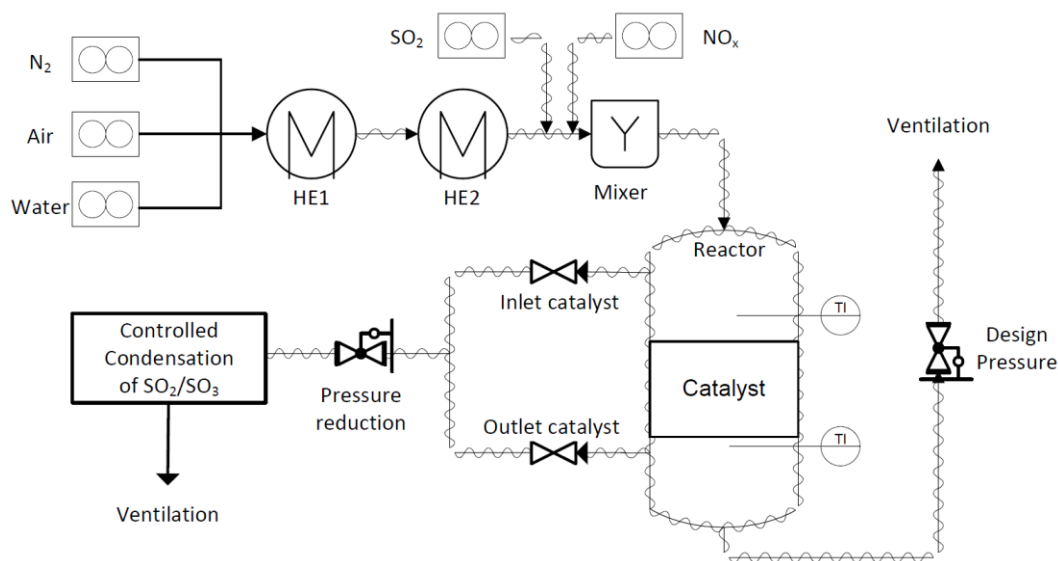


Fig. 2 Monolith reactor setup at Haldor Topsøe A/S

To reach steady state conditions, a conditioning period of 15-20 h must be used when measuring the oxidation of SO_2 . The long conditioning time is due to sulfating of the catalyst and is part of the mechanism behind SO_2 oxidation, involving adsorption of SO_2 , oxidation of SO_2 to SO_3 on the surface of the catalyst, and lastly the desorption of SO_3 ^{17,25,30}. To ensure sufficient conditioning time, the catalyst was left overnight after a change in temperature, species concentration, or pressure was introduced. Sufficient conditioning time was assumed when two measurements, with approximately 2-4 hours between each measurement, using the same conditions showed the same conversion of SO_2 . If this was not the case, the catalyst was left an additional day, and measurements were repeated.

Table 1 gives an overview of the performed experiments covering 2 different commercial maritime SCR catalysts. To clarify the direct pressure effects on reaction kinetics, similar residence times in the catalyst were imposed by increasing the total flow rate proportionally to the pressure. The residence time for the different conditions

is indicated by the linear velocity through the channels or by the weight based residence time (W/Q), where W is the mass of the catalyst element and Q is the total volumetric flow rate (1 bar, 0 °C), as shown in **Table 1**. As shown in Table 1 there were minor changes in the SO_2 inlet concentration when the pressure was varied, indicating offset in the actual total flow compared to the expected total flow. The total flow rate as shown in **Table 1**, was therefore calculated from the measured outlet SO_x concentrations and the flow rate of SO_2 added to the flue gas.

Table 1 The total flow rate and the linear velocity through the catalyst channels (at reaction pressure and 0 °C). The measured mean inlet concentration and the standard deviation based upon all measurements are also shown

<u>Catalyst</u>	<u>Pressure</u>	<u>Total Flow rate</u>	<u>Linear</u> <u>Velocity</u>	<u>Mean SO_2 Inlet</u> <u>Conc.</u>	<u>Weight Based</u> <u>Residence time</u>
	Bar	m^3/h @ 0 °C, 1 atm.	m/s @ 0 °C	ppm, dry	$kg_{cat} \cdot s/m^3$
0.66 L Low V- SCR	1	4.5	0.85	930 ± 15	119.1
0.66 L Low V- SCR	3	14.4	0.94	860 ± 15	107.3
0.66 L Low V- SCR	4.5	21.9	0.95	850 ± 15	106.0
0.34 L High V- SCR	1	2.6	0.48	1120 ± 15	97.5
0.34 L High V- SCR	2.9	8.5	0.55	980 ± 15	84.5

The outlet concentrations of SO_2 and SO_3 were measured using the controlled condensation method as described by the Topsøe method 1305³¹, which is a modification of the ASTM D-3226-73T standard method. The Topsøe method is based on controlled condensation of sulfuric acid at a temperature of 70 °C and subsequent titration of sulfate ions. At a temperature of 70 °C only sulfuric acid will condense, and since SO_2 has a very low solubility in sulfuric acid, SO_2 will be unaffected by the condensation. SO_2 is then subsequently collected in a 6% aqueous solution of H_2O_2 (converted into sulfuric acid). The collected samples are titrated with 0.005 M barium

perchlorate as titrant and thorin as an indicator, using a Metrohm 862 compact titrosampler.

2.2 Catalysts

The conversion of SO_2 into SO_3 was measured for two ternary (1.2 wt% or 3 wt% V_2O_5 / $\sim 10\%$ WO_3 / TiO_2) marine SCR catalyst (V-SCR) with a honeycomb structure supplied by Haldor Topsøe A/S. Both catalysts were cut into a square cross-sectional surface area (43.5 mm) to fit into the reactor and sealed with quartz wool as shown in **Fig. 3**.

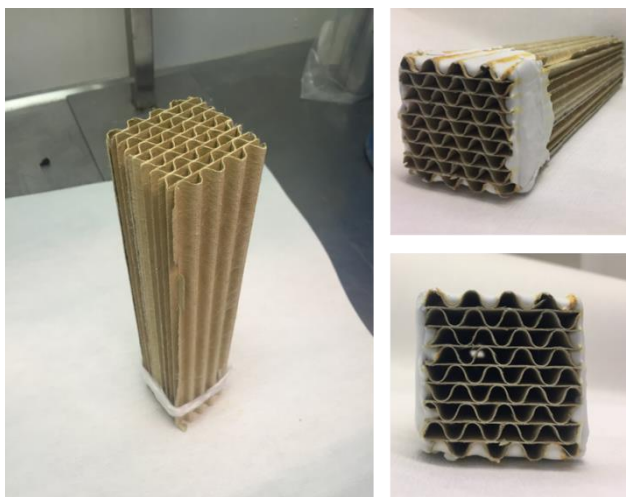


Fig. 3 Pictures of the high vanadia content SCR catalyst, with quartz wool in one end. It should be noted that the catalyst was fixed using quartz wool in both ends before loading

The catalyst was forced to fit into the reactor to ensure that no gas would bypass the catalyst. Further information on the catalyst properties can be found in Table 2. A roughly twice as large volume of catalyst was used for the low V-SCR catalyst to get a reasonable amount of SO_2 oxidation also at the lowest temperature of 300 °C.

Table 2 Characteristics of the tested catalysts

	Low V-SCR	High V-SCR
V_2O_5 Content – wt%	1.2	3
Width or Length – mm	43.6	43.5
Height – mm	460	231
Weight – g	145.7	69
# of open Channels	59	61

Hydraulic diameter – mm	4.3	4.3
Void - %	80	80

3 Results and Discussion

3.1 Pressurized SO₂ Oxidation

A background measurement was performed at 390°C, 1000 ppm SO₂, and 1 bar, by measuring the conversion of SO₂ at the inlet to the catalyst, which yielded a negligible SO₂ oxidation (0.07%). Consequently, the conversion of SO₂ into SO₃ could be measured by simultaneously measuring the SO₂ and SO₃ concentration out of the reactor. The sum of SO₂ and SO₃ out of the reactor was assumed to correspond to the inlet concentration of SO₂. The conversion of SO₂ was calculated based on the measured SO₃ concentration and the inlet concentration of SO₂.

The conversion of SO₂ was measured across a low V-SCR and a high V-SCR catalyst at temperatures and pressures relevant for marine SCR, i.e., 300-400°C and 1-4.5 bar and the results are shown in Fig. 4. The mean conversion of SO₂ is shown by the symbols in Fig 4 and is based upon two measurements. The two measurements used to calculate the mean are shown as the top and bottom point of the bar in each symbol.

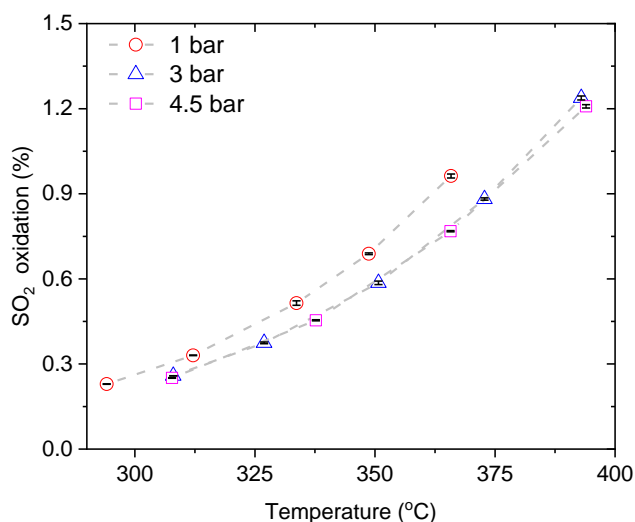


Fig. 4(a) Conversion of SO₂ for the Low V-SCR catalyst

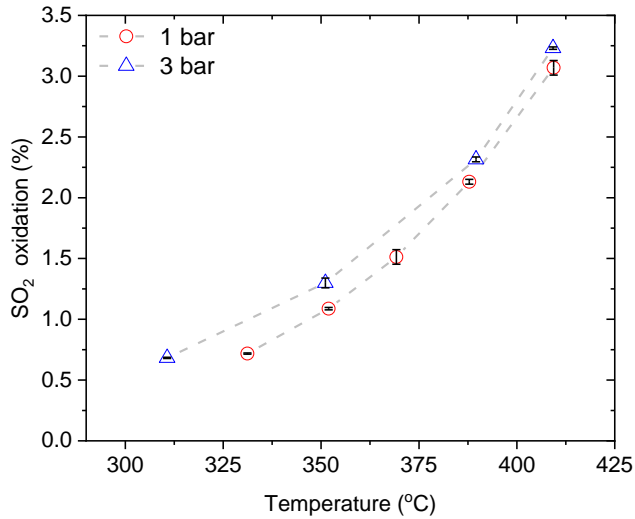


Fig. 4(b) Conversion of SO₂ for the High V-SCR catalyst

Fig. 4 The mean steady state SO₂ oxidation measured across two marine type commercial V-SCR catalysts. Symbols shows the mean, top and bottom of bar is the two measurements used to calculate the mean, and dashed lines connects each measurement. General test conditions were 5% H₂O, 8-10% O₂, SO₂ according to **Table 1** and balance N₂. It should be noted that the 3 bar test for the high V-SCR was performed with 2% H₂O as discussed in Section 3.2

Fig. 4 shows that when the residence time is kept constant, as is the case for 3 and 4.5 bar for the low V-SCR catalyst, according to **Table 1**, the measured conversion of SO₂ is identical, independent of the change in pressure, indicating pressure independent kinetics. **Fig. 4** shows that in general a higher conversion of SO₂ is found for the high V-SCR catalyst compared to the low V-SCR catalyst as has also been found in literature^{24,28}. The highest measured conversion of SO₂ is below approximately 1.2 % for the low V-SCR catalyst (Figure 4a) and 3.2 % for the high V-SCR catalyst (Figure 4b). For the high V-SCR catalyst the maximum value corresponds to an SO₃ concentration of around 30 ppm at a pressure of 3 bar. It should be noted that these levels of SO₂ conversion are far below the equilibrium conversion predicted by HSC chemistry 9.0® ($X_e(300 - 400^\circ\text{C}) \gg 95\%$) and therefore, the measured kinetics are not influenced by the reverse reaction. A similar conversion of SO₂ has also been reported by other authors in studies at atmospheric pressure^{8,17,32}. The two measurements performed at each steady state, as indicated by the top and bottom of the bars in each symbol shows that the double determination gave very similar results for the low V-SCR catalyst, indicating steady state conditions and good repeatability. For the high V-SCR catalyst (**Fig. 4b**) a higher uncertainty, compared to the low V-SCR catalyst, is observed. The measured conversion of SO₂ at the high V-SCR catalyst is higher at 3 bar, even though the residence time in

the catalyst is lower (by 12%) than the residence time at 1 bar, as also shown in **Table 1**, which is unexpected and must be due to uncertainties in the calculated/measured flow. The observed uncertainty is not considered prohibitively large and the results are useful and trustworthy.

3.2 SO₂ Oxidation and H₂O

Addition of water significantly decreases the SO₂ oxidation, but at practical water concentrations (≥ 5 vol% at atmospheric pressure) the rate of SO₂ oxidation is known to be independent of the water concentration^{8,25}. Therefore, experiments were in general performed with 5 vol% of water in the gas, however, MFC limitations during the 3 bar high V-SCR experiment yielded only 2 vol% of water. A repetition was, therefore, performed at 390°C and 3 bar, both with 2 vol% of water and 5 vol% of water in the gas to ensure that the results obtained with 2 vol% of water at 3 bar could be compared to the results using 5 vol% of water at 1 bar. **Fig. 5** shows the measured conversion of SO₂.

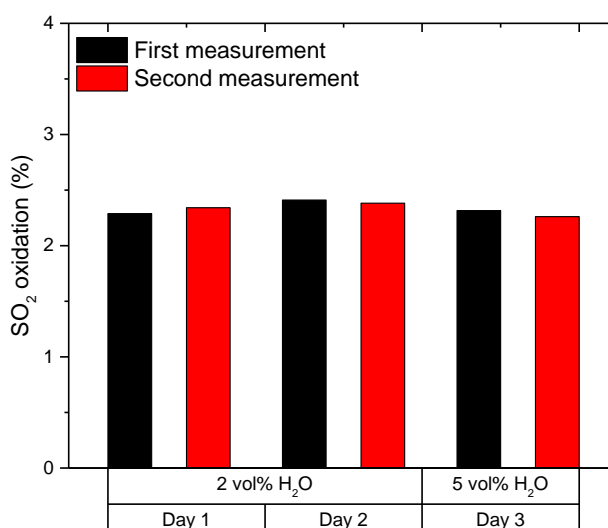


Fig. 5 Repetition of SO₂ oxidation at 390°C and 3 bar across the high V-SCR with 2 vol% and 5 vol% of H₂O

Fig. 5 shows that at a temperature of 390°C and a pressure of 3 bar, the measured conversion of SO₂ is independent of the water concentration when changing from 2 vol% of water to 5 vol% of water. Svachula et al.²⁵ also tested the inhibiting effect of water on SO₂ oxidation at atmospheric pressure and stated that the conversion of SO₂ is independent of water at concentrations above 5 vol% of water. The experiments presented here, are well in line with the results of Svachula et al., since the concentration of 2 vol% water at 3 bar corresponds to the same partial pressure as 6

vol% at 1 bar. Therefore, based on **Fig. 5** the results obtained using 2 vol% of water at 3 bar and the results obtained using 5 vol% of water at 1 bar are considered comparable.

3.3 SO₂ Inlet Concentration

The conversion of SO₂ was measured as a function of the inlet concentration of SO₂ at a temperature of 350°C at 1 and 3 bar for the low-V SCR catalyst. The inlet concentration of SO₂ was changed from the standard concentration of approximately 900 ppm to 1400 ppm of SO₂ at 1 bar and at 3 bar. At 3 bar an additional experiment was also performed with 400 ppm of SO₂. The conversion of SO₂ using the different inlet concentrations is shown in Fig. 6.

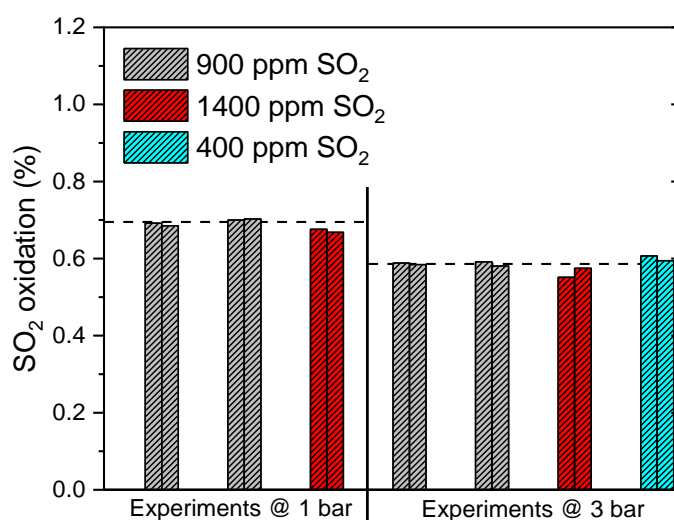


Fig. 6 The conversion of SO₂ with varying SO₂ inlet concentrations measured at 350°C at 1 and 3 bar. The dashed lines indicate the mean of the standard experiment using 900 ppm of SO₂

Fig. 6 shows that the conversion of SO₂ is independent of the SO₂ inlet concentration, indicating a first order reaction as discussed further below. It should be noted that the difference in the conversion of SO₂ observed at 1 bar and 3 bar, is due to a higher residence time at 1 bar, as already discussed and shown in Table 1, and hence the conversion of SO₂ should not be compared across pressure in Fig. 6.

3.4 SO₂ Kinetic Model

The extent of external and internal mass transfer limitation is estimated from the Carberry number, and the internal effectiveness factor (See Online Resources 1). On this basis the SO₂ oxidation was found to be kinetically controlled, as also reported by other authors^{17,25,29,32}, and therefore, the reaction will take place in the full monolith wall.

A reactor model assuming plug flow of gas through the channels, no transport limitations and an n'th order rate expression was applied when fitting the kinetic parameters, as shown in equation (6). The rate expression on the right hand side of equation (6) assumes a zero reaction order in oxygen which has been reported by other authors under conditions where the oxygen concentration is above 2 vol%²⁵, which is the case for all experiments presented here and typical ship engine out concentrations²⁷.

$$F_{SO_2,0} \cdot \frac{dX}{dW} = -r_{SO_2} = k \cdot p_{SO_2}^\alpha \cdot p_{SO_3}^\beta \quad (6)$$

In equation (6) $F_{SO_2,0}$ is the molar feed rate of SO_2 , W is the mass of catalyst and X is the conversion of SO_2 . The rate constant was fitted using a modified Arrhenius equation, as shown in Equation (7).

$$k(T) = k(T_{ref}) \cdot \exp\left(\frac{-E_a}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \quad (7)$$

In which $k(T_{ref})$ is the rate constant at a reference temperature, which was chosen at 350°C, a midpoint in the investigated temperature interval. This way of formulating the rate constant minimizes the correlation between the pre-exponential factor and the activation energy³³. The four variables, $k(T_{ref})$, E_a , α , and β were fitted by minimization of the residual sum of square (RSS), as given in Equation (8), using the function “lsqcurvefit” in Matlab®.

$$RSS = \sum_i (y_{calc} - y_{exp})^2 \quad (8)$$

The goodness of a fitting result is evaluated based on the residual mean square error (RMSE) which is the RSS value divided by the number of data points.

3.5 Fitting Results

The first fitting was done for the low V-SCR catalyst where changes in the inlet SO_2 concentration were performed at 1 bar and 3 bar, which made it possible to fit both rate constant, activation energy and the reaction orders at each pressure as shown in **Table 3**.

Table 3 The results of fitting at individual pressures across the low V-SCR catalyst, where changes in the inlet SO_2 concentration was performed, see Section 3.3

Low V-SCR Catalyst	

Pressure bar	k(350°C) mol/(kg*s*Pa ⁿ)	E _a kJ/mol	α	β	RMSE
1 bar	0.092·10 ⁻⁶	53.2	0.77	0.14	3.45·10 ⁻⁵
3 bar	0.092·10 ⁻⁶	50.3	0.78	0.18	6.13·10 ⁻⁵

The low RMSE values in **Table 3** indicate a good fit. However, the fitting solutions depended on the initial guess, due to too few data points. The solutions shown in Table 4, were the ones giving the lowest RMSE while still keeping similar reference rate constants and activation energies at the two pressures. The results shown in **Table 3** show that the reaction rate parameters did not significantly change when changing the pressure, and therefore, the datasets were merged into one dataset for each catalyst and refitted as shown in **Table 4**.

Table 4 Results of fitting the merged data for each catalyst. Red entries are forced and therefore not fitted

Low V-SCR Catalyst					High V-SCR Catalyst				
k(350°C) mol/(kg*s*Pa ⁿ)	E _a kJ/mol	α	β	RMSE	k(350°C) mol/(kg*s*Pa ⁿ)	E _a kJ/mol	α	β	RMSE
0.092·10 ⁻⁶	50.7	0.78	0.16	1.05·10 ⁻⁴	0.040·10 ⁻⁶	49.7	1.08	0.16	4.28·10 ⁻³
0.040·10 ⁻⁶	60.5	0.91	0	1.28·10 ⁻⁴	0.016·10 ⁻⁶	59.2	1.25	0	4.41·10 ⁻³
0.025·10 ⁻⁶	57.2	1	0	1.07·10 ⁻³	0.053·10 ⁻⁶	63.4	1	0	0.545·10 ⁻¹

The fitting of the merged dataset for the low V-SCR catalyst resulted in solutions that were independent of the initial guess, and as expected the goodness of the fit was poorer as shown by the RMSE values in Table 4 compared to **Table 3**. **Table 4** also shows fitting results for the merged dataset for the high V-SCR catalyst. Entry 1, in Table 4, shows that when all four parameters were fitted, it resulted in a slightly positive value for the reaction order of SO₃ (β) for both catalysts. Dunn et al.²⁴ tested a series of binary catalysts (1-7 wt% V₂O₅/TiO₂) and found that the reaction order of SO₂ could only be fitted as a first order when a negative first order was assumed for SO₃. Dunn et al. observed as high as 10% SO₂ conversion, resulting in an SO₃ concentration of around 100 ppm. However, since Dunn et al. performed atmospheric experiments, the partial pressure of SO₃ corresponds to about the same value as obtained at elevated pressure in the experiments presented here. A negative first order dependency of SO₃ was not found in this work, but rather a value close to zero. Since the reaction order of SO₃ was found close to zero it was assumed to be zero and the other three parameters refitted.

Based on a zero order dependency of SO₃ (β=0), the fitted reaction order of SO₂ (α) was close to 1 for the low V-SCR as shown in Table 4 entry 2. Experiments with variation in

inlet SO₂ concentration was only performed using the low V-SCR catalyst, making that dataset better suited for fitting of reaction orders. The small positive reaction order of $\alpha=1.25$, found for the high V-SCR catalyst is considered close to one, since the fractional higher order does not seem physical. Based on these fitting results, the reaction order of SO₂ is in general found close to 1, and hence for practical purposes, a first order dependency can be used, also for increased pressures of up to 4.5 bar. A practical first order dependency was also proposed by Svachula et al.²⁵ for atmospheric pressures.

The proposed first order dependency of SO₂, and a zero order dependency on SO₃, resulted in an activation energy of 57.2 kJ/mol and a reference rate constant at 350°C of $0.025 \cdot 10^{-6}$ mol/(kg*s*Pa) for the low V-SCR catalyst and 63.4 kJ/mol and a reference rate constant at 350°C of $0.053 \cdot 10^{-6}$ mol/(kg*s*Pa) for the high V-SCR catalyst. The reference rate constant for the high V-SCR is 2.1 times higher than that for the low V-SCR catalyst. This indicates that the rate of SO₂ oxidation scales roughly linearly with the V-content since the high V-SCR catalyst contains 2.5 times more active material (3 wt% vs. 1.2 wt%). Similar activation energies have also been reported by other authors^{28,30}, however, higher activation energies have also been reported, i.e., Beeckman et al.²⁹ with an activation energy of 110 kJ/mol.

In **Fig. 7** the measured conversion of SO₂ is plotted against that calculated based upon the kinetics assuming first order in SO₂ and zero order in SO₃ as shown in **Table 4**.

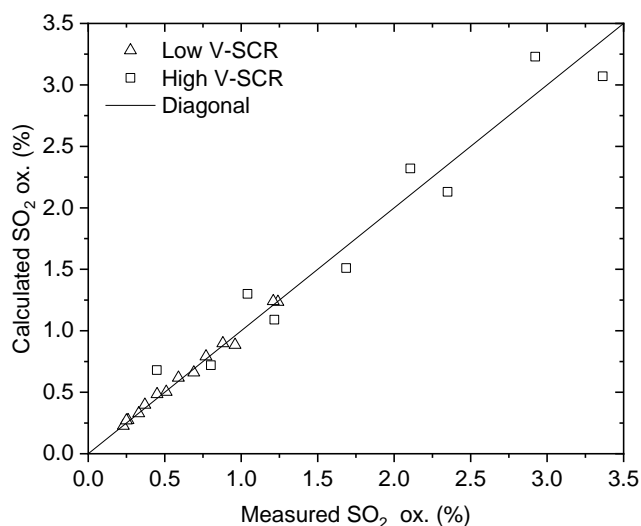


Fig. 7 A parity plot, showing how well the final kinetics fits the measured data. A good fit is indicated by points on the diagonal

Fig. 7 shows that there is a good agreement between the fitted and measured data for the low V-SCR catalyst. For the high V-SCR catalyst a poorer agreement is observed which was also expected, based on the uncertainty observed in the dataset.

3.6 Fitted Kinetics Compared to Literature Values

SO₂ oxidation kinetics have been found in the literature, and for comparison, the natural logarithm of the rate of reaction is shown in **Fig. 8** together with the kinetics found in this study. Full kinetic expressions are sparse in the literature, so the data shown in **Fig. 8** are based on rate plots found in the literature, which were read off as [X,Y] points by use of “plot digitizer³⁴” and transformed into the same units i.e., mol/(m³_{cat}·s). For instance in Beeckman et al.²⁹ the first order rate constant is found in units of cm/s, which are changed based on the supplied catalyst volume specific surface area, $SS=1.23 \cdot 10^6 \text{ cm}^2/\text{cm}^3$ ²⁹, and using first order in SO₂ with an initial concentration of 1000 ppm SO₂.

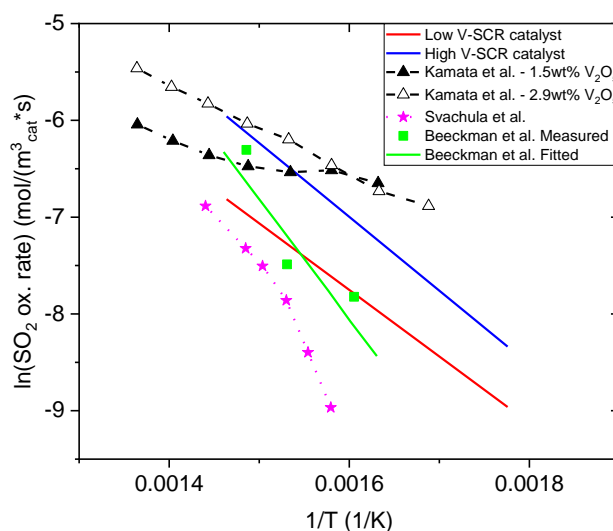


Fig. 8 The rate of SO₂ oxidation, based on kinetics fitted to first order in SO₂ and zero order in SO₃ at 1000 ppm SO₂ and compared to kinetics found in the literature by Kamata et al.²⁸, Svachula et al.²⁵, and Beeckman et al.²⁹

Fig. 8 shows that the kinetics found in this study are similar to those found in the literature^{25,28,29}. Kamata et al.³⁵ studied SO₂ oxidation on grounded binary catalysts with various loading of V₂O₅ on TiO₂ in an atmosphere of 500 ppm SO₂, 7500 ppm O₂, and balance N₂. The fact that no WO₃ was present in the catalyst and no water in the gas phase compared to the results presented here, would be expected to result in a higher rate, although this is not apparent from **Fig. 8**. A possible reason could be that Kamata et al. did experiments with a low oxygen concentration, where the rate can be limited by

the lack of oxygen ($O_2 < 2\%$ ²⁵). Kamata et al. observed similar rates at temperatures lower than 600 K for catalysts with 1.5wt% or 2.9wt% V_2O_5 , which is likely due to difficulties in measuring the very low rate, especially because, Kamata et al. measured the conversion of SO_2 by evaluating the consumption of SO_2 , and not the formation of SO_3 directly.

Beeckman et al.²⁹ tested a commercial catalyst, with 0.4 wt% V_2O_5 on TiO_2 in an atmosphere of 400 ppm NO, 400 ppm NH_3 , 1000 ppm SO_2 , 4% O_2 and 10% H_2O . Beeckman et al. do not state whether WO_3 is part of the catalyst. However, one could speculate that WO_3 (or MoO_3) is present since it is commonly added to commercial vanadium based SCR catalyst, to suppress the SO_2 oxidation³⁶ and suppress the transformation of TiO_2 , from the high surface area form of anatase to rutile³⁷. With the presence of both NO and NH_3 and the possible lack of WO_3 and less V_2O_5 in the catalyst makes it hard to speculate on whether or not a similar rate should be expected. Ammonia in the gas is reported to decrease the rate of SO_2 oxidation^{25,32} and is kinetically modelled as a competitive adsorption on the surface of the catalyst. However, none of the studies comment on the sulfate formation which happens when NH_3 and SO_3 is present in the gas. Formation of sulfates could decrease the measured conversion of SO_2 , but not necessarily the SO_2 oxidation itself. For instance, Orsenigo et al.¹⁷ reported a decrease in measured SO_3 when ammonia was added to the exhaust gas, however, they also detected a maximum concentration of SO_3 after ammonia was added, after which the SO_3 levels then returned to its original values in a matter of 8 hours. The maximum could be due to decomposition of sulfates. Studies including NH_3 and taking into account sulfate formation should be performed.

The rate of SO_2 oxidation reported by Svachula et al.²⁵ was measured using 1000 ppm SO_2 , 2% O_2 , 10% H_2O and balance N_2 on commercial V-SCR catalyst. As with Beeckman et al. the presence of WO_3 in the commercial catalyst is not stated, and the V_2O_5 concentration is stated to be low, within a possible range of 0.3-2 wt% V_2O_5 that Svachula et al. investigated. The low V_2O_5 concentration, should result in a lower rate of SO_2 oxidation compared to the results from this study, which is clear in **Fig. 8**. Svachula et al. reported a change in activation energy within the investigated temperature interval ($T=360-420^\circ C$), and compared it to those typically found for vanadium based sulfuric acid catalyst. However, vanadium present in sulfuric acid catalysts are known to be in the liquid molten state³⁸ which is not the case for the vanadium based SCR catalyst, hence the break is unexpected, and not observed for the catalyst used here.

3.7 SO₂ Oxidation in the presence of NO_x

SO₂ oxidation was also studied across the low V-SCR catalyst with 1000 ppm of NO_x present in the gas at 1 and 3 bar and an additional experiment was performed with 1000 ppm NO, and 400 ppm NO₂ at 3 bar. NO_x was added as pure NO, however, small amounts of the NO can be oxidized to NO₂ before and within the catalyst especially at increased pressure (not measured), and the term "NO_x addition" is therefore used. When both NO and NO₂ were added, a NO₂ generator was used, in which NO and air were mixed using an over-stoichiometric ratio of oxygen and allowed to react at room temperature in a long Teflon tube. The NO₂ generator is known from previous tests by Haldor Topsøe A/S to result in conversions above 95% of NO to NO₂. When 400 ppm of NO₂ was added, it is under the assumption of 100% NO conversion in the NO₂ generator. NO, and NO₂ are added separately to the hot gas, and subsequently mixed. In SCR experiments not reported here with a similar residence time 1-2 ppm of NO₂ was present at atmospheric pressure and 6-8 ppm of NO₂ at 3 bar. The oxidation of NO is believed to follow a second order dependency in NO, hence increasing the NO concentration (by increasing the pressure from 1 to 3 bar), more than doubles the NO₂ concentration³⁹.

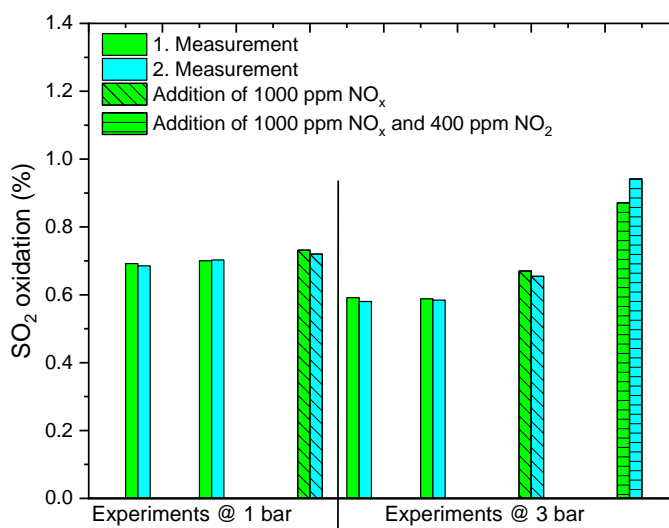


Fig. 9 SO₂ oxidation measured at 350°C at 1 and 3 bar across the low V-SCR catalyst without NO_x, with 1000 ppm NO_x, and with 400 ppm NO₂ and 1000 ppm NO_x. Beside NO_x standard conditions as shown in **Table 1** was used

Fig. 9 shows a small increase of 4.5 % in the conversion of SO₂ when 1000 ppm of NO_x was added to the gas mixture at 1 bar indicating a small promoting effect of NO_x. However, the small relative increase of 4.5% compared to the 1.8% of difference

between the two repetitions is considered too small to give a definite conclusion. At 3 bar and when 1000 ppm of NO_x was added, the conversion of SO₂ increased from 0.59% to 0.66% SO₂ oxidation, i.e., an increase by 12 %, which is expected to be due to a catalyzed reaction between SO₂ and NO₂ according to reaction (9). To further investigate if the increased oxidation was due to a reaction with NO₂, an additional amount of 400 ppm of NO₂ was added, which increased the conversion of SO₂ with 54% compared to without NO_x, from 0.59% to a mean of 0.91% SO₂ oxidation.



Measurements performed by Orsenigo et al.¹⁷, showed that the promoting effect of NO_x on the conversion of SO₂ was only observed when a catalyst was present, indicating that the gas phase reaction is negligible. The lack of gas phase reaction was also confirmed by calculations using a detailed chemical kinetic model of the gas phase reactions⁴⁰ at 400°C, 1 bar, 1000 ppm NO₂ and 3000 ppm SO₂. Orsenigo et al.¹⁷ suggested that the promoting effect could be explained by an over oxidation of the V-SCR catalyst, however, in this study it is explained by reaction (9) being catalyzed by the V-SCR catalyst, since this reaction thermodynamically should be possible ($\Delta G^\circ = -35 \frac{\text{kJ}}{\text{mol}}$)⁴¹. Earlier studies^{17,25,32} have all reported a promoting effect of NO_x measured at atmospheric pressures. However, in these studies, NO_x and air were mixed at room temperature and subsequently heated together which can cause an increased formation of NO₂ since the NO oxidation in air has a negative activation energy ($E_a/R = -530 \pm 400\text{K}$)³⁹ and therefore will be limited at increased temperature. This also explains why the addition of NO_x at 1 bar in the experiments presented in this paper only gives a small promoting effect because NO is added directly to the hot (300-400°C) feed gas, and hence, only at elevated pressure a substantial amount of NO₂ is expected.

4 Conclusion

The following conclusions can be drawn from this study of SO₂ oxidation at pressures up to 4.5 bar across two commercial marine V-SCR catalysts with either 'low' or 'high' vanadium content:

- The oxidation of SO₂ is found to be kinetically limited in the temperature interval relevant for SCR operation (300-425 °C).

- The measured conversion of SO₂ into SO₃ across the commercial catalysts is of the order 0.2-3 %, with no influence of pressure when the residence time was constant. This shows that the kinetics is independent on the pressure in the investigated range.
- The catalyst with the higher vanadium content was more active for SO₂ oxidation.
- The kinetics of the reaction was fitted, and the reaction orders were found to be close to one for SO₂ and zero for SO₃. For practical purposes, it is therefore proposed that the reaction order is approximated by a first order dependency in SO₂ and a zero order dependency in SO₃ also at pressures up to 4.5 bar.
- The rate of SO₂ oxidation was found independent of water concentrations above 2 vol% at 3 bar, in correspondence with previous findings that the rate is independent of the water concentration above 5 vol% at 1 bar.
- The fitted kinetics are well in line with those found in the literature measured at atmospheric pressure.
- The rate of SO₂ oxidation was clearly promoted by the presence of NO_x at increased pressure, however, at 1 bar the promoting effect was within experimental uncertainty. The promoting effect is explained by a catalyzed redox reaction between SO₂ and NO₂.

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Conflict of Interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

Abbreviations

ABS	Ammonium bisulfate
AS	Ammonium sulfate
EGR	Exhaust gas recirculation

HE	Heat exchanger
MFC	Mass flow controller
NECA	NO _x emission control area
NO _x	Nitrogen oxides
RMSE	Residual mean square error
RSS	Residual sum of squares
SCR	Selective catalytic reduction
SECA	SO _x emission control area
SO _x	Sulfur oxides
V-SCR Catalyst	Vanadium based SCR catalyst

Symbols

α	Reaction order of SO ₂ []
β	Reaction order of SO ₃ []
E_a	Activation Energy [kJ/mol]
$F_{a,0}$	Molar feed rate of component a [mol/s]
G°	Gibbs free energy at 25°C
$k(T_{ref})$	SO ₂ rate constant at temperature T_{ref}
p_a	Partial pressure of component a [Pa]
Q	Total volumetric flow rate [m ³ /h]
SS	Specific surface area of catalyst
T_{ref}	Reference temperature for SO ₂ rate expression [K]
W	Mass of catalyst [kg]
X	Conversion []
X_e	Equilibrium conversion []

y_{calc}

Calculated SO₂ conversion

y_{exp}

Measured SO₂ conversion

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